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PROCESS FOR PREPARING MIXTURES OF LOW-FOAMING, NONIONIC
SURFACTANTS WITH AN ACETAL STRUCTURE

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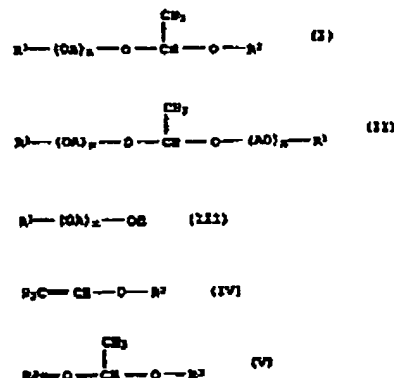
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Abstract

The invention concerns the production of mixtures of low-foaming non-ionic surfactants with an acetal structure, the mixtures containing: A) 70 to 99 % by wt. of one or more unsymmetrical acetals (I) in which R^1 is a C_1 - C_{30} alkyl group, a C_2 - C_{30} alkenyl group or a C_7 - C_{30} aralkyl or alkaryl group, R^2 is a C_1 - C_{10} alkyl group, A is a 1,2-alkylene group with 2 to 4 C-atoms and x can take values from 1 to 50; and B) 1 to 30 % by wt. of one or more symmetrical acetals (II) in which R^1 , A and x are as defined above, by reacting alkoxylates (III) $R^1-(OA)_x-OH$ with vinyl ethers (IV) $H_2C=CH-O-R^2$ in the presence of protonic acids or Lewis acids as catalysts, the reaction being carried out in the presence of one or more acetaldehyde dialkylacetals (V), in which R^3 is a C_1 - C_{10} alkyl group and R^2 and R^3 may be the same or different, in an amount corresponding to 0.1 to 20 moles of the compounds of formula (V) per mole of the compounds of formula (III) or in the presence of protonic acids as catalysts, the catalysts used being organic acids with a pK_a -value of 1 to 7 for the first dissociation stage of the acids in water.



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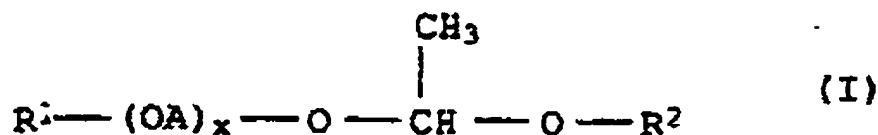
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Description

The present invention pertains to an improved process for the preparation of mixtures of low-foaming, nonionic surfactants with an acetal structure, which contain

A) 70 to 99 wt% of one or more asymmetrical acetals of general formula I



in which

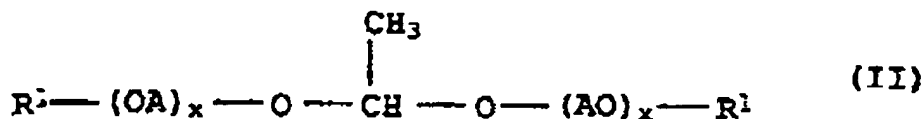
R^1 designates a C_1 to C_{30} alkyl residue, a C_3 to C_{30} alkenyl residue, or a C_7 to C_{30} aralkyl or alkaryl residue,

R^2 signifies a C_1 to C_{10} alkyl residue,

A stands for a 1,2-alkylene group with 2 to 4 C atoms, and

x can assume values of 1 to 50, and

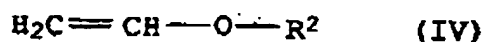
B) 1 to 30 wt% of one or more symmetrical acetals of general formula II



in which the variables R^1 , A, and x have the meanings designated above, by reacting alkoxylates of general formula III



with vinyl ethers of general formula IV

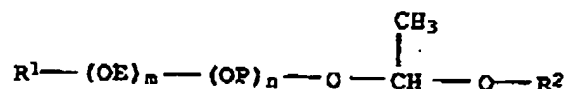


in the presence of acids as catalysts.

Since part of these surfactant mixtures represents new substances, the present invention also pertains to these new mixtures.

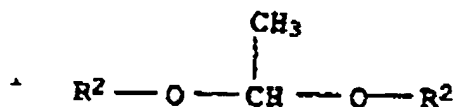
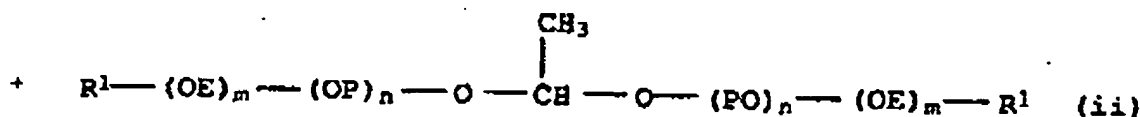
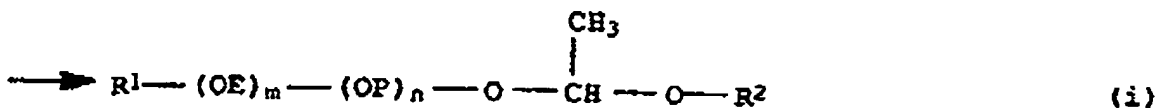
Nowadays, washing and cleaning processes in industry, commercial plants, and households increasingly require surface active substances that excel, on the one hand, in particular by virtue of their stability with respect to alkalis, their low-foaming character, and their effective foam attenuation and which, on the other hand, stand out by virtue of their rapid and total biodegradability.

Alkyl alkoxyates with an acetal structure have been proposed during the search for compounds that meet these requirements, e.g. compounds of the following type were proposed in DE-A 22 52 186 (1):



whereby R^1 designates a long-chain saturated or unsaturated alkyl residue or alkylaryl residue, E signifies ethylene and P signifies propylene, m and n can be a number from 1 to 30 or 5 to 50, R^2 represents a shorter alkyl chain with 1 to 10 carbon atoms or a residue with the formula $R^1-(EO)_m-(PO)_n$.

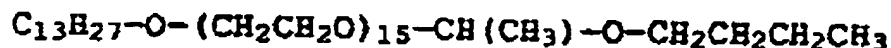
The preparation of such acetals is described in the above unexamined patent application via catalysis by means of strong Bronsted acids or Lewis acids, whereby mention is made of the fact that different products are obtained as a result of varying the temperature:



Thus product (i) is preferentially formed at temperatures $<30^\circ\text{C}$, whereas product (ii) is formed at increasing temperatures in the case of temperatures $>30^\circ\text{C}$.

US-A 3,244,753 (2) pertains to the reaction of alkyl alkoxyates with vinyl ethers via catalysis by means of strong Bronsted acids with use being made of an addition of phosphorus-containing acids for the purpose of color lightening; however, the reaction is quantified only via the OH number, and the composition of the various acetal products is not given.

Example 1 of this US patent specification describes the preparation of the following compound

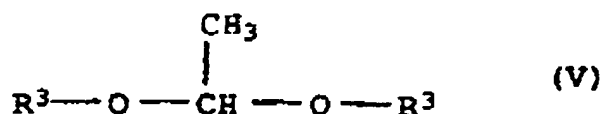


by reacting an ethoxylated tridecyl alcohol with n-butyl vinyl ether in the presence of catalytic quantities of p-toluenesulfonic acid and hypophosphorous acid at 35 to 40°C; in this way, the acetal is obtained in a yield of 94% with a light color.

The problem for the present invention was therefore to make available an inexpensive and simple process with which the reacetalization of compound I to give compound II is largely avoided, and compound I is obtained in high yields, and a light-colored product is produced. This objective is based on the fact that compounds of type I exhibit significantly better biodegradability than compounds of type II.

For economic reasons, it is also desirable that use be made of only one catalyst that simultaneously steers the reaction in the desired direction and thereby generates a light-colored product.

The process that was defined at the beginning, in the presence of Bronsted acids or Lewis acids as catalysts, has accordingly been found, whereby this process is characterized by the feature that the reaction is carried out in the presence of one or more acetaldehyde dialkylacetals of general formula V



in which R^3 designates a C_1 to C_{10} alkyl residue, and whereby R^2 and R^3 can have the same or different meanings, using quantities of 0.1 to 20 mol of the compounds V per mol of III.

Surprisingly, it has now been found that the yield of the desired products I can be increased significantly as a result of the addition of the compounds V that also serve in practice as solvents in this connection. On the other hand, the situation is then reached that the reaction temperature can be increased by approximately 20°C to >30°C during the exothermic reaction, and thus expensive and energetically unfavorable cooling of the reaction mixture can be avoided during operational implementation.

The acetaldehyde dialkylacetals V that are used as solvents and reaction partners can be prepared with ease from the corresponding alkyl vinyl ether and alkyl alcohol using acid catalysis at 50 to 100°C. The problem of reacetalization - which arises because the alkyl residues are similar in nature - and hence the production of a mixture of products does not occur in the case of

this preparatory procedure. The acetaldehyde dialkylacetals V are formed virtually quantitatively during this reaction, and are obtained in yields of >95% after neutralization and distillation. After the reaction, the acetaldehyde dialkylacetals V, which are used for the acetalization of the alkoxylates III to give the products I, can be separated with ease by means of distillation, and they can be used again without problems in several synthesis cycles. This is a significant advantage relative to an excess of alkyl vinyl ether as proposed in (1) since this excess of vinyl ether - which produces impurities, e.g. [simple] acetal formations - cannot be used again without reservation.

The cyclic, or preferably acyclic alkyl residues R^3 of the acetaldehyde dialkylacetals V can contain 1 to 10, or preferably 1 to 4 C atoms. Consideration can be given, in particular, to branched C_3 or C_4 alkyl residues for this purpose, and the isobutyl residue is quite especially suitable. Those acetaldehyde dialkylacetals V in which R^3 has the same meaning as R^2 , i.e. it is the same as the alkyl residue in the vinyl ethers IV, are also preferred.

The use of acetaldehyde dialkylacetals V has the advantage that the reaction temperature for the reaction of III with IV can be increased to 30 to 80°C, or preferably 35 to 70°C, and especially 40 to 60°C. This leads, on the one hand, to the feature that expensive cooling is eliminated during implementation of the reaction and, on the other hand, to the feature that possible viscosity problems are avoided that arise in particular at temperatures of <30°C during this reaction without solvents.

In a preferred embodiment of the process, the acetaldehyde dialkylacetal V is introduced into the reaction vessel; the vinyl ether IV and, separately, a mixture comprising the alkoxylate III and the catalyst are then added simultaneously. In this way, one ensures that the vinyl ether IV immediately reacts to completion with the alcohol to give the desired product I and, as a result, unnecessary discoloration of the product is avoided that otherwise arises, via polymerization reactions, as a result of a local excess of the vinyl ether in the presence of a high concentration of acid.

The molar ratio of acetaldehyde dialkylacetal V to alkoxylate III amounts to 0.1:1 to 20:1, or preferably 0.5:1 to 10:1. If one does not want to obtain mixtures in regard to the alkyl chain - which is preferable - then the alkyl residue R^3 in V must, of course, be identical to the alkyl residue R^2 in the alkyl vinyl ether III that is used. If, however, mixtures in regard to this alkyl residue are possible and desired, then acetaldehyde dialkylacetals V and alkyl vinyl ethers III with different alkyl residues can be used as well. The alkoxylate III and the alkyl vinyl ether IV are usually used in equimolar or approximately equimolar amounts. An excess of vinyl ether IV is not necessary in order to achieve large quantities of I.

The process that was defined at the beginning, in the presence of Bronsted acids as catalysts, has also been found, whereby this process is characterized by the feature that, as

catalysts, use is made of organic acids with a pK_s value of 1 to 7, based on the first dissociation stage of the acids in water.

Surprisingly, it has been found that reacetalization with the formation of the symmetrical acetals II can be largely suppressed during the reaction of the alkoxylates III with the vinyl ethers IV as a result of using weak organic acids such as these, and hence the asymmetrical acetals I become available in high yields. Surprisingly, it has also been found that the reaction is capable of being carried out at higher temperatures than the reaction with strong organic acids, mineral acids, or Lewis acids. This leads to the feature that solvents can be eliminated that, in practice, have to be added at temperatures of $<30^\circ\text{C}$ because of the frequently elevated viscosity. Strong discoloration of the product, which occurs with ease in the case of strong mineral acids, Lewis acids, or strong organic acids at elevated temperatures ($> 50^\circ\text{C}$), is no longer observable, either.

The weak organic acids that are used and that can also contain additional functional groups, such as hydroxyl groups, carbonyl groups, nitrile groups, olefinic double bonds, aryl residues or halogen atoms, are acids with pK_s values of 1 to 7, and preferably 1.2 to 5, and especially 1.5 to 4, based on the first dissociation stage of the acids in water. In particular, these organic acids are carboxylic acids. The following can be designated as examples: oxalic acid, citric acid, nitrilotriacetic acid, tartaric acid, fumaric acid, terephthalic acid, malic acid, propionic acid, salicylic acid, succinic acid, glutaric acid, adipic acid, acrylic acid, methacrylic acid, lactic acid, phthalic acid, malonic acid, benzoic acid, acetic acid, formic acid, α -halogenocarboxylic acids, e.g. chloroacetic acid or dichloroacetic acid, propiolic acid, citraconic acid, and maleic acid. The following are preferred among these: formic acid, acetic acid, oxalic acid, citric acid, tartaric acid, phthalic acid, terephthalic acid, fumaric acid and, in particular, malic acid.

As a rule, the catalysts are neutralized by means of a conventional base after the reaction has taken place.

No additional catalyst component is required except the designated weak organic acids in order to achieve the desired effects, especially the production of light-colored products.

The catalyst concentration hereby lies in the conventionally used range and, as a rule, amounts to 0.1 to 10 mol%, or preferably 0.3 to 7 mol%, and especially 0.5 to 5 mol%, based on the vinyl ether IV that is used.

The reaction temperature when using the designated weak organic acids is normally 50 to 150°C , and preferably 60 to 130°C , and especially 70 to 100°C .

As a rule, the reaction is carried out in such a way that the vinyl ether component is introduced into the reaction vessel and mixed with the weak organic acids as the acid catalyst. Heating to the reaction temperature then takes place, and the alkoxylate component is added. Stirring for times of 0.25 to 20 h usually follows, depending on the acid strength and the acid concentration of the catalyst that is used. As a rule, however, times of subsequent stirring of only

0.25 to 5 h are necessary, in the case of the preferred use of maleic acid, subsequent stirring times of 0.25 to 1 h are necessary. The reaction can also be carried out inversely, i.e. by introducing the alkoxylate or the alkoxylate/catalyst mixture into the reaction vessel, and then adding the vinyl ether/catalyst mixture or the vinyl ether. The alkoxylate component and the vinyl ether component are usually used in equimolar or approximately equimolar amounts. An excess of vinyl ether is not required in order to achieve large quantities of the asymmetrical acetal I.

The following can be designated, by way of example, as the straight-chain or branched alkyl and alkenyl residues R^1 : n-hexyl, n-heptyl, n-octyl, 2-ethylhexyl, n-nonyl, isononyl, n-decyl, isodecyl, n-undecyl, n-dodecyl, n-tridecyl, iso-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-octadecyl, n-eicosyl, oleyl, linolyl, and linolenyl. The residues R^1 are preferably of the straight-chain type, or are branched only to a small extent, i.e. they contain maximally 3 methyl or ethyl side chains.

Depending on the origin of the alcohol that is used in the synthesis, the R^1 residues are residues in naturally occurring fatty alcohols, or preferably synthetically prepared oxo alcohols or Ziegler alcohols. Examples of alcohols that are prepared in accordance with the oxo synthesis and that are readily usable are C_{10} , C_{13} , and C_{15} alcohols as well as C_9/C_{11} , C_{10}/C_{12} , C_{12}/C_{14} , C_{13}/C_{15} , and C_{16}/C_{18} alkanol mixtures. Examples of alcohols that are prepared in accordance with the Ziegler synthesis and that are readily usable are C_8/C_{10} , C_{10}/C_{12} , C_{12}/C_{14} , C_{12}/C_{16} , C_{16}/C_{18} , and C_{16}/C_{20} alkanol mixtures.

Since the alcohols that are used in the synthesis are generally random mixtures of homologs and isomers, it is expedient to speak of the average number of C atoms in the residues R^1 .

Alkyl or alkenyl residues with 8 to 20 C atoms, and especially those with 10 to 18 C atoms, are preferred for R^1 . Residues R^1 that have their origin in the C_{10} fraction, the C_{13} fraction, the C_{10}/C_{12} fraction, the C_{12}/C_{14} fraction, the C_{13}/C_{15} fraction, or the C_{16}/C_{18} fraction of alcohols that are obtained in accordance with the oxo synthesis are especially advantageous.

The variable R^1 can also stand for aralkyl residues, especially phenylalkyl residues or alkaryl residues, and especially alkylphenyl residues, preferably with a total of 8 to 20 C atoms in each case. Examples of these are: benzyl, β -phenylethyl, 4-phenylbutyl, ω -phenyldecyl, ω -phenyldodecyl, o-tolyl, m-tolyl, p-tolyl, o-ethylphenyl, m-ethylphenyl, p-ethylphenyl, o-butylphenyl, m-butylphenyl, p-butylphenyl, p-decylphenyl or p-dodecylphenyl.

The 1,2-alkylene groups A designate, in particular, the ethylene group and also, in addition, the propylene group, the 1,2-butylene group, and the 2,3-butylene group. In this regard, each group A can also designate a random mixture of several of the designated 1,2-alkylene groups, or a group that is assembled from up to three uniform blocks of these alkylene groups; however, 1,2-alkylene groups A are preferred that contain only one single constitutional unit.

The degree of alkoxylation x preferably is 2 to 15, and especially 3 to 12, whereby these numbers are to be regarded as average values for random distributions of the alkoxylation products.

The cyclic, or preferably acyclic alkyl residues R^2 of the vinyl ethers IV that are used can contain 1 to 10, or preferably 1 to 4 C atoms. Branched C_3 or C_4 alkyl residues can be considered in particular in this regard; the isobutyl residue is quite especially suitable.

The following are suitable as catalysts for the reaction of III with IV: Lewis acids, such as e.g. BF_3 , $SbCl_3$, or $TiCl_4$, strong mineral acids, such as e.g. hydrochloric acid (especially in its anhydrous version in the form of hydrogen chloride), sulfuric acid, or phosphoric acid, or strong organic acids, such as e.g. trifluoromethanesulfonic acid, methanesulfonic acid, trifluoroacetic acid, dodecylbenzenesulfonic acids, or toluenesulfonic acids.

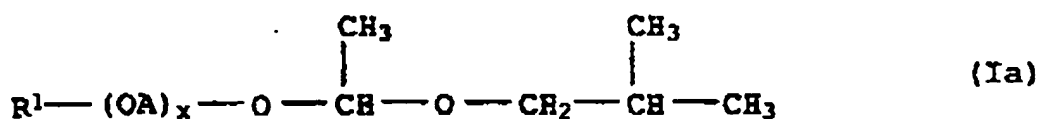
The following are preferred among these: hydrochloric acid, sulfuric acid, phosphoric acid, methanesulfonic acid, benzenesulfonic acid, p-dodecylbenzenesulfonic acid, and, in particular, p-toluenesulfonic acid. These catalysts are used in quantities that are conventional for this purpose. No additional catalyst component is required in order to achieve the desired effects, especially in order to achieve light-colored products.

As a rule, the catalysts are neutralized by means of a conventional base after the reaction has taken place.

Reaction implementation in accordance with the invention leads to mixtures of products that preferably contain the asymmetrical acetal I. These product mixtures preferably contain 75 to 98 wt% of the compounds I, and 2 to 25 wt% of the compounds II, especially 80 to 95 wt% of I, and 5 to 20 wt% of II, and particularly 83 to 92 wt% of I, and 8 to 17 wt% of II, when using acetaldehyde dialkylacetals, or 82 to 94 wt% of I, and 6 to 18 wt% of II when using weak organic acids as catalysts. In addition, for example, small quantities of acetaldehyde dialkylacetals can also be present, whereby these acetaldehyde dialkylacetals are formed during the reacetalization of I to give II. A preponderance of I leads to improved biodegradability of the products. At the same time, the products are stable with respect to alkalis, they are low-foaming, and they are especially suitable for cleaning processes with high mechanical stresses, e.g. when washing culinary utensils, or for commercial bottle washing.

A subject of the present invention also comprises mixtures of low-foaming, nonionic surfactants with an acetal structure, which contain

A) 70 to 99 wt% of one or more asymmetrical acetals of general formula Ia



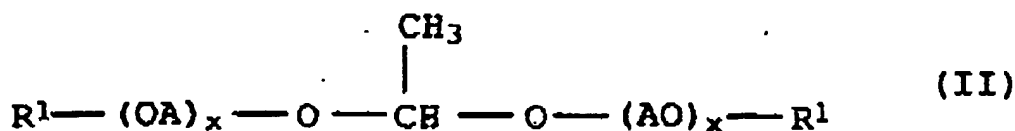
in which

R^1 designates a C_1 to C_{30} alkyl residue, a C_3 to C_{30} alkenyl residue, or a C_7 to C_{30} aralkyl or alkaryl residue,

A stands for a 1,2-alkylene group with 2 to 4 C atoms, and

x can assume values of 1 to 50, and

B) 1 to 30 wt% of one or more symmetrical acetals of general formula II



in which the variables R^1 , A, and x have the meanings designated above.

These mixtures exhibit especially good technical application properties.

The following examples will describe in greater detail the process in accordance with the invention.

Preparation of acetaldehyde diisobutylacetal

37 g (0.5 mol) of isobutanol were introduced into a flask, and mixed with 0.657 g (0.003 mol) of p-toluenesulfonic acid. Heating to 60°C was done, and 50 g (0.5 mol) of vinyl isobutyl ether were added with stirring over a period of 1 h. Stirring for a further 30 min was then done at 60°C, followed by neutralization by means of Na_2CO_3 , filtration, and distillation under normal pressure. The yield amounted to 84 g (96.9%)

Example 1

200 g of acetaldehyde diisobutylacetal were introduced into a flask, and heated to 40°C with stirring. 4.9 g of p-toluenesulfonic acid were separately mixed with 326 g (0.5 mol) of a fatty alcohol ethoxylate (a C_{12} - C_{18} fatty alcohol mixture reacted with 10 mol of ethylene oxide). 50 g (0.5 mol) of vinyl isobutyl ether and the fatty alcohol ethoxylate/catalyst mixture were then simultaneously added to the flask over a period of 2 h. Stirring was carried out for a further 30 min after the end of the addition, followed by neutralization by means of Na_2CO_3 , and filtration, and the excess acetaldehyde diisobutylacetal was largely distilled off under the vacuum that was

produced by a jet of water from a faucet. 380 g of a clear, colorless product were obtained. The composition is given in Table 1 below together with that from the additional examples.

Examples 2 and 3

100 g or 300 g of acetaldehyde diisobutylacetal were used analogously to Example 1.

Comparative Example A

50 g (0.5 mol) of vinyl isobutyl ether were introduced into the flask, and heated to 40°C; the fatty alcohol ethoxylate/catalyst mixture described in Example 1 was added over a period of 2 h. After a subsequent time of stirring of 30 min, neutralization and filtration, a product was obtained that was dark brown in color.

Comparative Example B

50 g (0.5 mol) of vinyl isobutyl ether and the fatty alcohol ethoxylate/catalyst mixture described in Example 1, were simultaneously added to the flask, namely dropwise at 40°C. For technical reasons, effective stirring could be carried out in this case only after 10% of the 2 hour addition time. Processing was done analogously to Example 1.

Comparative Example C

The fatty alcohol ethoxylate/catalyst mixture described in Example 1 was introduced into the flask, and vinyl isobutyl ether was added dropwise over a period of 2 h. Processing was done analogously to Example 1.

Comparative Example D

100 g of methyl tert-butyl ether were introduced into the flask, mixed with 50 g (0.5 mol) of vinyl isobutyl ether, and then allowed to stand at 20°C. The fatty alcohol ethoxylate/catalyst mixture described in Example 1 was added to this mixture over a period of 2 h. Processing was done analogously to Example 1.

Comparative Example E

Example D was repeated at 40°C.

Comparative Example F

100 g of methyl tert-butyl ether were mixed with 4.9 g of p-toluenesulfonic acid and allowed to stand at 20°C. The fatty alcohol ethoxylate and vinyl isobutyl ether were added,

individually and simultaneously, over a period of 2 h. Processing was done analogously to Example 1.

Comparative Example G

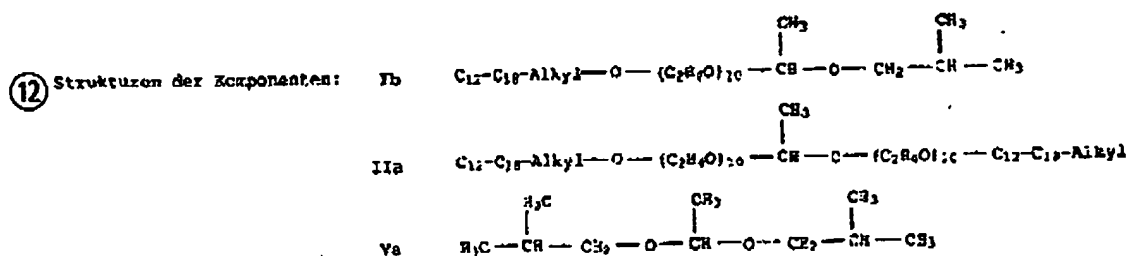
Analogously to Example 1, the corresponding quantities of acetaldehyde diisobutylacetal, isobutyl vinyl ether, and p-toluenesulfonic acid were introduced into the flask at 20°C, and then the fatty alcohol ethoxylate was added. Increasingly strong discoloration of the product was observed during the addition. This was also observed if the acetaldehyde diisobutylacetal was omitted as the solvent.

Comparative Example H

Analogously to Example 1, the corresponding quantities of acetaldehyde diisobutylacetal and p-toluenesulfonic acid were introduced into the flask and the corresponding quantities of the fatty alcohol ethoxylate and vinyl isobutyl ether were added, individually but simultaneously, at 20°C. Strong discoloration of the product was observed during the addition.

(A) Tabelle 1
Zusammensetzungen und Ergebnisse

Beispiel Nr. (1)	Temperatur [°C] (2)	OH-Zahl [mg KOH/g] (3)	Ib [Gew.-%] (4)	IIa [Gew.-%] (5)	Va [Gew.-%] (6)	Farbe (7)
1	40	4,7	88,5	10,0	1,5	farblos (8)
2	40	5,4	89,8	8,4	1,8	farblos
3	40	3,8	85,1	12,1	2,8	farblos
A	40	6,5	54,8	37,3	7,8	dunkelbraun (9)
B	40	5,5	65,0	29,2	5,8	gelb (10)
C	40	6,5	53,5	37,5	9,0	gelb
D	20	6,4	78,0	20,3	1,7	hellgelb (11)
E	40	6,1	61,3	35,0	3,7	gelb
F	20	6,4	67,3	27,7	5,1	dunkelbraun
G	20	6,0	77,2	18,2	4,5	dunkelbraun
H	20	5,3	79,7	17,8	3,1	dunkelbraun



- Key: A Table 1
Compositions and results
- 1 Example No.
2 Temperature [°C]
3 OH number [mg KOH/g]
4 Ib [wt%]
5 IIa [wt%]
6 Va [wt%]
7 Color
8 Colorless
9 Dark brown
10 Yellow
11 Light yellow
12 Structure of the components:

Example 4

75 g (0.75 mol) of vinyl isobutyl ether were introduced into a flask and mixed with 4 g (0.035 mol) of maleic acid. The mixture was heated to 70°C. 480 g (0.75 mol) of an addition product comprising a C₁₂-C₁₈ fatty alcohol mixture with 9.5 mol of ethylene oxide (OH number: 89 mg KOH/g) were added over a period of 1 h with intense stirring, whereby the temperature was increased to 80°C. Stirring was carried out for a further 30 min at 80°C after the addition had ended; neutralization was done by means of 10.5 g (0.07 mol) of triethanolamine, followed by filtration. After removing the readily volatile components using the vacuum that was produced by a jet of water from a faucet, 542 g of a light-colored product were obtained that was as clear as water and whose composition is given in the following table.

Examples 5 through 9

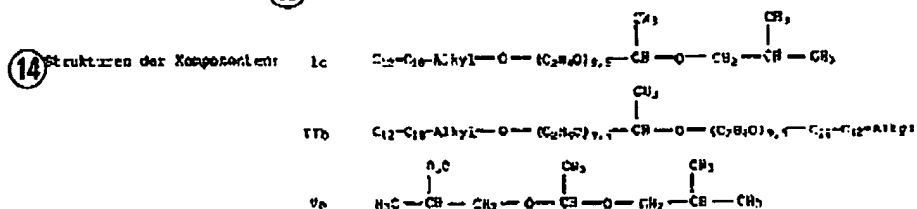
Analogously to Example 4, use could also be made, as catalysts, of the additional organic acids that are given in Table 2 below. In each case, colorless products were obtained that were as clear as water and whose compositions can be seen in the following table.

Comparative Examples J and K

Analogously to Example 4, use was made of 3.8 g (0.02 mol) of p-toluenesulfonic acid or 1.96 g (0.02 mol) of phosphoric acid. After neutralization, the products were dark brown to black in color.

A Tabelle 2
Zusammensetzungen und Reaktionsparameter

1 Beispiel Nr.	2 Katalysator (pK _s -Wert)	3 Umsetzungs-temperatur [°C]	4 Nachrührzeit (h)	5 Verbindung (Gew.-%)		
				IIb	IIa	V
4 6	Maleinsäure (1,92)	80	2,0	88,9	8,7	2,3
5 7	Citronensäure (5,38)	96	13,0	93,7	5,5	0,8
6 8	Oxalsäure (1,23)	85	5,25	82,3	13,4	4,4
7 9	D,L-Tartronsäure (2,99)	96	6,5	91,1	7,7	1,2
8 10	Formonsäure (3,75)	96	7,0	92,6	5,8	1,6
9 11	Acetonsäure (4,75)	96	9,0	92,2	6,9	1,6
10 12	p-Toluolsulfonsäure (1-6,5)	70	0,25	54,2	37,9	8,6
11 13	Phosphorsäure (2,15)	70	0,25	49,8	39,7	10,4

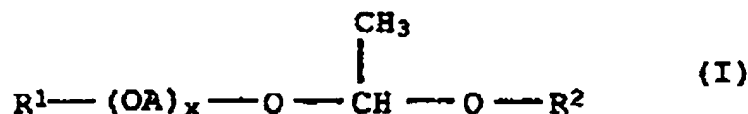


- Key: A Table 2
Compositions and reaction parameters
- 1 Example No.
2 Catalyst (pK_s value)
3 Reaction temperature [°C]
4 Time of subsequent stirring [h]
5 Compound [wt%]
6 Maleic acid
7 Citric acid
8 Oxalic acid
9 D,L-tartaric acid
10 Formic acid
11 Acetic acid
12 p-toluenesulfonic acid
13 Phosphoric acid
14 Structure of the components:

Claims

1. Process for the preparation of mixtures of low-foaming, nonionic surfactants with an acetal structure, which contain

A) 70 to 99 wt% of one or more asymmetrical acetals of general formula I



in which

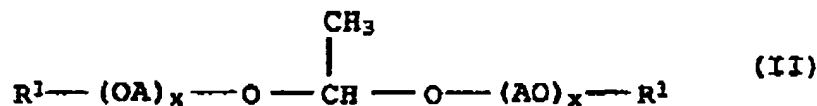
R^1 designates a C_1 to C_{30} alkyl residue, a C_3 to C_{30} alkenyl residue, or a C_7 to C_{30} aralkyl or alkaryl residue,

R^2 signifies a C_1 to C_{10} alkyl residue,

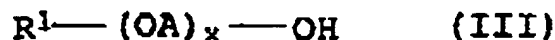
A stands for a 1,2-alkylene group with 2 to 4 C atoms, and

x can assume values of 1 to 50, and

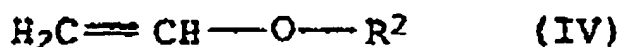
B) 1 to 30 wt% of one or more symmetrical acetals of general formula II



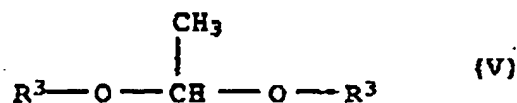
in which the variables R^1 , A, and x have the meanings designated above,
by reacting alkoxylates of general formula III



with vinyl ethers of general formula IV



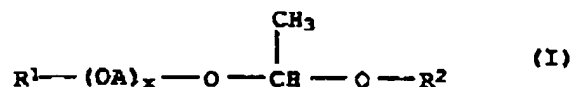
in the presence of Bronsted acids or Lewis acid as catalysts, characterized by the feature that the reaction is carried out in the presence of one or more acetaldehyde dialkylacetals of general formula V



in which R^3 designates a C_1 to C_{10} alkyl residue, whereby R^2 and R^3 can have the same or different meanings, using a quantity of 0.1 to 20 mol of the compounds V per mol of III.

2. Process for the preparation of mixtures of low-foaming, nonionic surfactants with an acetal structure, which contain

A) 70 to 99 wt% of one or more asymmetrical acetals of general formula I



in which

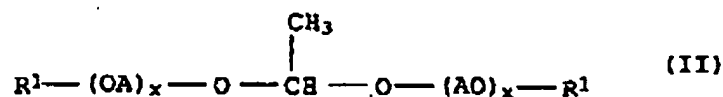
R^1 designates a C_1 to C_{30} alkyl residue, a C_3 to C_{30} alkenyl residue, or a C_7 to C_{30} aralkyl or alkaryl residue,

R^2 signifies a C_1 to C_{10} alkyl residue,

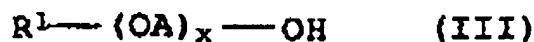
A stands for a 1,2-alkylene group with 2 to 4 C atoms, and

x can assume values of 1 to 50, and

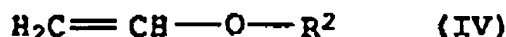
B) 1 to 30 wt% of one or more symmetrical acetals of general formula II



in which the variables R^1 , A, and x have the meanings designated above, by reacting alkoxylates of general formula III



with vinyl ethers of general formula IV



in the presence of Bronsted acids as catalysts, characterized by the feature that, as the catalysts, use is made of organic acids with a pK_a value of 1 to 7, based on the first dissociation stage of the acids in water.

3. Process for the preparation of mixtures of low-foaming, nonionic surfactants with an acetal structure in accordance with Claim 1 or 2 that contain

A) 80 to 95 wt% of the compounds I, and

B) 5 to 20 wt% of the compounds II.

4. Process for the preparation of mixtures of low-foaming, nonionic surfactants with an acetal structure in accordance with Claims 1 through 3, whereby the variable R^1 in the compounds I and II designates a C_8 to C_{20} alkyl residue or a C_8 to C_{20} alkenyl residue.

5. Process for the preparation of mixtures of low-foaming, nonionic surfactants with an acetal structure in accordance with Claims 1 through 4, whereby the variable R^2 in the compounds I designates a branched C_3 or C_4 alkyl residue.

6. Process for the preparation of mixtures of low-foaming, nonionic surfactants with an acetal structure in accordance with Claims 1 through 5, whereby the variable A stands for an ethylene group, and the variable x can assume values of 2 to 15.

7. Process for the preparation of mixtures of low-foaming, nonionic surfactants with an acetal structure in accordance with Claim 1, characterized by the feature that use is made of those acetaldehyde dialkylacetals V in which the variable R³ has the same meaning as R².

8. Process for the preparation of mixtures of low-foaming, nonionic surfactants with an acetal structure in accordance with Claim 1 or 7, with use being made of hydrochloric acid, sulfuric acid, phosphoric acid, methanesulfonic acid, benzenesulfonic acid, p-toluenesulfonic acid, or p-dodecylbenzenesulfonic acid as the catalyst.

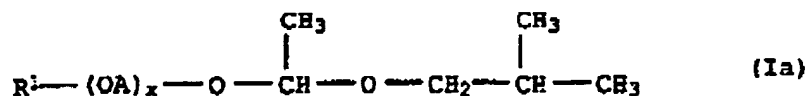
9. Process for the preparation of mixtures of low-foaming, nonionic surfactants with an acetal structure in accordance with Claim 1, 7, or 8 as a result of carrying out the reaction at a temperature of 30 to 100°C.

10. Process for the preparation of mixtures of low-foaming, nonionic surfactants with an acetal structure in accordance with Claim 1, or 7 through 9, characterized by the feature that the acetaldehyde dialkylacetal V is introduced into the reaction vessel, and the vinyl ether IV and a mixture comprising the alkoxylate III and the catalyst are then added simultaneously.

11. Process for the preparation of mixtures of low-foaming, nonionic surfactants with an acetal structure in accordance with Claim 2, characterized by the feature that use is made of formic acid, acetic acid, oxalic acid, citric acid, tartaric acid, phthalic acid, terephthalic acid, fumaric acid, or maleic acid as the catalysts.

12. Process for the preparation of mixtures of low-foaming, nonionic surfactants with an acetal structure in accordance with Claim 2 or 11 at a temperature of 50 to 150°C.

13. Mixtures of low-foaming, nonionic surfactants with an acetal structure, which contain
A) 70 to 99 wt% of one or more asymmetrical acetals of general formula Ia



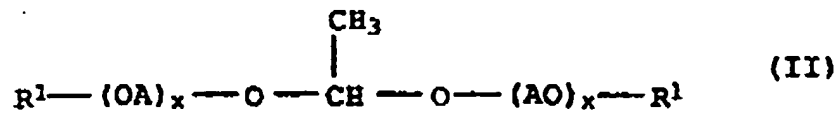
in which

R¹ designates a C₁ to C₃₀ alkyl residue, a C₃ to C₃₀ alkenyl residue, or a C₇ to C₃₀ aralkyl or alkaryl residue,

A stands for a 1,2-alkylene group with 2 to 4 C atoms, and

x can assume values of 1 to 50, and

B) 1 to 30 wt% of one or more symmetrical acetals of general formula II



in which the variables R^1 , A, and x have the meanings designated above.

INTERNATIONAL SEARCH REPORT

 Int. Application No.
 PCT/EP 94/03631

 A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C07C43/315 C1101/72 C08G65/32 C07C41/54

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

 Minimum documentation searched (classification system followed by classification symbols)
 IPC 6 C07C C08G C110

Documentation searched other than originating documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base used, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE,A,22 52 186 (BASF) 16 May 1974 see the whole document, cited in the description	1-13
A	US,A,3 244 753 (R. E. LEARY) 5 April 1966 see the whole document, cited in the description	1-13
A	GB,A,1 052 301 (ROHM & HAAS) 7 April 1964 see claims; example 1	1-13
A	EP,A,0 514 652 (BASF) 25 November 1992 see page 3, line 23 - line 26; claims	1-13

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

28 December 1994

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Int. Application No.

PCT/EP 94/03631

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		CA-A- 776153	
		FR-A- 1395977	
		NL-A- 6404098	19-10-64
EP-A-0514652	25-11-92	DE-A- 4113163	05-11-92
		JP-A- 5117197	16-05-93
		US-A- 5206443	27-04-93

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